Free Radical Reactions within Tropospheric Aqueous Particles: Indications for Changes in Gas Phase Oxidation Capacity

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Results from recent photochemical and kinetic laboratory and modelling studies of the formation and reactivity of aqueous phase free radicals such as NO_3, SO_4^-, Br_2^- and Cl_2^- will be presented. Laser-based methods have been applied for the specific generation and time-resolved detection of the above transient species in systematic studies. Photolytic radical generation in solution, radical phase transfer, radical interconversion reactions and the influence of organic compounds on the chemistry within the aqueous tropospheric phase will be discussed. Results indicate that solution reactions of the above radicals may significantly influence the net effects of chemistry within droplets and aerosols dispersed in air.

A multiphase box model coupling an advanced aqueous phase mechanism (CAPRAM 2.2) to the established RADM 2 mechanism is applied to quantify effects of multiphase conversions. It will be demonstrated for different cases that aqueous phase processes do not only alter the oxidation capacity of the tropospheric gas phase by uptake of trace gases but that aqueous multiphase systems actively change gas phase radical budgets e.g. by the conversion of OH into halogen atoms by solution free radical reaction sequences beyond the level currently discussed in literature. Specific differences between the current understanding of cloud chemistry and aerosol chemistry will also be discussed.